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PATENT SPECIFICATION

(11) 1 507 454

1 507 454

- (21) Application No. 20826/74 (22) Filed 10 May 1974
 (21) Application No. 32743/74 (22) Filed 24 July 1974
 (23) Complete Specification filed 19 June 1975
 (44) Complete Specification published 12 April 1978
 (51) INT CL⁷ D21H 5/10; B32B 33/00; B41M 3/14//D21H 1/34
 (52) Index at acceptance

B6A 42A 42D

B6C 301 320 33X AP

- (72) Inventors PETER ROBERT STEINER, PETER SINCLAIR and
 GEOFFREY SIMON KEEP



(54) SECURITY PAPER

(71) We, WIGGINS TEAPE LIMITED, a British Company, of Gateway House, Basing View, Basingstoke, Hampshire RG21 2EE, England, (formerly of 3 Lincoln's Inn Fields, London WC2A 3EB), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of authenticating a document and to, in combination, a document to be authenticated and an authenticating composition.

It is desirable for certain documents to be authenticatable by an addressee or recipient of the documents. Examples of such documents are cheques, postal orders and bearer bonds, which authorise the issuance or crediting of money or value to a bearer, and also such items as entrance or other tickets, passes, passports and letters of authority which afford the bearer a particular right, such as access to a restricted area or the redemption of deposited property.

Such documents are normally printed on special paper, referred to herein as "security paper," which includes features by means of which the paper can be easily identified, for example by a counter clerk or stadium gateman. The use of such paper guards against the possibility of counterfeiting. The paper may be identified by, for example, the presence of special watermarks, and/or metallic or plastic strips embedded in the paper. These features are normally such as can only be introduced during the paper manufacture, and so can not easily be introduced into readily-available papers. Additional security features can be introduced subsequently when the paper is printed, for example by the printing of elaborate designs, and the use of special inks.

In practice, such techniques have only been partially successful in preventing counterfeiting, and in any case, they frequently rely on lengthy examination procedures which are impracticable at, for example, a busy bank or Post Office counter or a box office. Moreover, features such as watermarks, included strips and elaborately printed designs can easily be studied by an intending counterfeiter, and he can readily ascertain what features he must emulate. It would clearly be desirable to provide a security paper in which the manner in which the security feature arose was not readily apparent.

It is an object of the present invention to provide a method of authenticating a document, wherein the document is printed on a security paper in which the aforementioned disadvantages are obviated or at least reduced.

The present invention is based on the reaction between a leucodye derivative and an acidic material, e.g. a phenolic resin, an organic acid or an acidic clay, to produce a coloured dye. Such a leucodye derivative will hereafter be referred to as a leucodye colour former. Leucodye colour formers are widely used in pressure-sensitive copying papers and are described in numerous patents on such papers. They will not therefore be discussed further herein.

It will be appreciated that a paper base coated with a leucodye colour former and a binder will have some security characteristics, in that if treated with an acidic co-reactant solution a colour will be developed. However, in authenticating a document it is frequently desirable to stamp some characters on the document, for example the date, or the name of the office at which the document is presented, rather than merely applying a blob of acidic co-reactant solution. Such characters can most conveniently be applied by means of a metal or rubber stamp applying an ink from a stamp pad. Application of acidic co-reactant solution

is also conveniently carried out by means of a stamp and a stamp pad impregnated with acidic co-reactant solution.

Pigmented black or other dark ink is frequently used for stamping characters on to documents, but if such an ink is used in conjunction with an acidic co-reactant solution for stamping a leucodye colour former coated security paper, the pigmented ink tends to obscure the colour developed by the colour former/co-reactant reaction. This problem might be overcome by the use of an ink based on a coloured dye, rather than on dark pigments, since the coloured dye developed by the authenticating colour former-co-reactant reaction would mingle with the dye in the ink and produce a further colour, for example a purple colour would result from a red ink and a blue developed dye. In contrast, a counterfeit paper would only bear the red colour of the ink.

However, in practice such a system suffers from the disadvantage that each time a document is authenticated, the stamp picks up a small amount of colour former which has just reacted with the co-reactant on the stamp to produce a coloured dye, i.e. the authenticating colour, and this dye is then transferred back to the stamp pad. In time, the stamp pad becomes appreciably contaminated with the dye, and security is lost, since the authenticating colour will appear on the paper being stamped regardless of its authenticity.

It is an object of the invention to obviate or at least to mitigate the aforementioned disadvantages, and to provide a method of authenticating a document, wherein the document is printed on a security paper and is authenticated using a stamp pad impregnated with a composition containing both an acidic coreactant and a pigmented dark ink.

According to a first aspect of the invention, there is provided a method of authenticating a document, wherein the document is printed on a security paper comprising a paper base coated with a composition containing a leucodye colour former, an inert filler and a binder, and is authenticated by stamping with an authenticating composition comprising a mixture of a pigmented dark ink and a solution of an acidic material which reacts with the leucodye colour former to develop a colour.

According to a second aspect of the invention, there is provided, in combination, a document to be authenticated and an authenticating composition which can be applied by stamping so as to produce a distinctive marking to authenticate said document, wherein the document is printed on a security paper comprising a paper base coated with a composition containing a leucodye colour former, an inert filler and a binder, and the authenticating composition comprises a mixture of a pigmented dark ink and a solution of an acidic material which reacts with the leucodye colour former to develop a colour.

The present invention is based on the discovery that once a stamping operation has taken place, the solution of co-reactant material spreads relatively quickly outwards from the point of application of the stamp and develops a colour in the region over which the co-reactant solution has spread, whereas the pigmented ink is retained at the place of application, probably as a consequence of adsorption on to the particles of filler. The resulting image on the paper is thus a dark impression surrounded by a coloured "halo." The presence of this "halo" constitutes the security feature which appears only when authenticity of the paper is tested.

If filler is not present, and a generous quantity of co-reactant solution is applied, the co-reactant solution might slowly spread outward from the point of application, and a faint halo might develop, but the speed and intensity of such development of a halo would be slow compared with the speed and intensity of halo development when a filler is present. It is thought that the enhanced speed and intensity of halo development observed with the present paper is the result of changes in the porosity of the paper resulting from the presence of filler in the coating composition on the paper.

The colour former/filler/binder composition may be coated by various conventional coating techniques, for example air-knife coating. Certain coating compositions may however give rise to problems with certain coating techniques, for example a high solids content coating composition may not be coatable at a size press without a poor coating pattern being produced, but the choice of a suitable coating technique is well within the competence of a skilled coating technologist.

The coat weight used obviously depends on economic as well as technical factors, in that for a cheap product it must be as small as possible. We have found

that a coat weight of 3-4 g/m² is suitable, since below this halo development is weaker than desirable and above this, as well as being more expensive, the problem of dusting becomes worse (the problem of dusting will be described subsequently).

As an additional security feature, the coating composition may be applied by spot printing instead of by air-knife coating. The spot printing may be selective, in that it would not cover all the sheet, or two colour formers with binder and filler can be applied to adjacent areas of the sheet. This would afford the possibility of a multi-coloured halo, and thus increase the difficulty of counterfeiting the present paper.

The coating composition may include one or more security chemicals to give protection against forgery (by forgery is meant the fraudulent alteration of a genuine security document, in contradistinction to counterfeiting which is the fraudulent production of security documents). Such security chemicals, the chemical composition of which are necessarily confidential, include that sold as "Vulcafor" (Registered Trade Mark), which gives rise to a brown stain on contact with bleach eradicators for removing fountain pen ink, and so-called solvent-sensitive dyes, which give rise to blue or black speckled stains on the application of solvent eradicators for removing ball-point pen ink. The use of solvent-sensitive dyes may impart a further security feature to the present security paper, in that the solvent for the acidic co-reactant material may develop the colour of the dye and thus give rise to a "halo" which contains dark specks. This may occur for example with benzyl alcohol as the solvent. Care must be exercised in choosing the security chemical(s) because they may not be compatible with all the binders or other mix constituents which may be used.

The binder used in the coating composition may be conventional, for example it may be a starch, casein or latex binder. Casein is preferable however, for reasons which will be discussed hereafter.

It is clearly desirable for the "flash-up" time of the halo to be near instantaneous as possible, since otherwise valuable time is wasted in waiting for the halo to appear. Thus it is important to select a colour former and co-reactant which react very rapidly with one another to develop a colour. The quickest halo is obtained if the paper has a high porosity, so that the acidic co-reactant solution spreads rapidly outwards from the point of application. However, such a paper is not really suitable for receiving fountain pen ink, since the ink tends to feather. Moreover, since the paper has to be printed to produce a security document, it is desirable that there should be as little "dusting" as possible ("dusting" is a well known phenomenon in the printing and paper coating industries and is a term used to denote separation of particles of fibre or coating composition from the body of the coated paper during or prior to printing. Such particles tend to adhere to printing apparatus, which results in a steady build-up of debris on the printing apparatus and thus in poor printing quality). Dusting can be reduced by increasing the amount of binder in the coating composition, but this in turn may result in a slower flash-up time. It is thus desirable to produce a coating which affords an acceptably short flash-up time whilst not being over-susceptible to ink feathering or to dusting.

It has been found that the choice of binder is one of the factors which influences the susceptibility of the paper to dusting, and that casein is preferable to conventional starch binders from this point of view. We have found that levels of casein from 12 to 13 parts of casein to 100 parts of filler provide a good compromise between coating adhesion, i.e. absence of dusting, and halo flash-up time.

As previously mentioned the binder may alternatively be a latex, for example a styrene acrylic co-polymer emulsion, for example those sold by Revertex Ltd. as Vinacryl 7170 and Vinacryl 7172, but it has been found that such latices appear to be no better and sometimes worse as regards dusting than a starch binder.

In conventional papers, calendering tends to reduce dusting, but we found that calendering at about 100 pli produced an increase in the flash-up time although it did produce a small improvement in dusting resistance. Choice of an acceptable compromise between calendering and flash-up time usually depends on the time available for authenticating the paper in use.

Suitable colour formers for use in the coating composition in the present security paper includes the following:

lactams, e.g. Rhodamine B lactam; phthalide derivatives, e.g. Crystal Violet Lactone; thiazine derivatives, e.g. benzoyl leuco methylene blue; oxazine derivatives, e.g. 3,7-bis(diethylamino)-10-benzoyl-phenoxazine; leucauramine

derivatives, e.g. bis(p-dimethylaminophenyl), n-hydroxyl ethyl piperiziny; diphenylamine derivatives, e.g. 4,4'-bis(dimethylamino)diphenylamine; pinacol derivatives, e.g. tetrakis(4-dimethylaminophenyl)ethanediol; spirodipyrans derivatives, e.g. 3-heptylbenzo[1,2-f]2H-chromene-2-spiro-2'-benzo[1,2-f]2H-chromene; fluoran derivatives, e.g. 3-chloro-6-cyclohexylaminofluoran and 2-di-benzyl-amino-6-dimethylamino-4-methyl fluoran; and fluoran lactam derivatives e.g. spiro 2-(2-chlorophenyl)phthalimido-3,9'-3',6'-bis(diethylamino)xanthene.

It has been found that the smaller the particle size of colour former, the more intense the developed colour produced. However, colour former particle size appears to have no direct effect on the halo flash-up time. The optimum particle size of colour former has so far been found to be 3-4 μ m, and this may be obtained by attrition, for example in a Torrance (Registered Trade Mark) IS attritor. Such a particle size does not necessarily give the most intense or most rapid halo development, but represents a compromise between halo development and the increased energy consumption and time taken by continued attrition. By using a colour former particle size of 3-4 μ m, it had been found that the proportion of colour former in the mix may be considerably reduced compared with that required for colour formers of larger particle size.

Suitable acidic co-reactant solutions for authenticating the present security paper include solutions of the following:—

sulphonic acids, e.g. benzene sulphonic acid, toluene-p-sulphonic acid, 2-naphthol-3,6 disulphonic acid, 1-naphthol-4-sulphonic acid, sulphanilic acid and sulphamic acid; carboxylic acids, e.g. d-tartaric acid, lactic acid, malonic acid, formic acid, citric acid, chloracetic acid, acetic acid, benzoic acid, tannic acid, succinic acid, stearic acid, adipic acid, p-toluic acid, and maleic acid; heteropoly acids, e.g. dodecap-tungstophosphoric acid, and dodeca-tungstosilicic acid; transition metal salts having some acidic character e.g. nickel chloride, zinc chloride, zinc nitrate, zinc bromide, zinc iodide, ferric chloride, cobaltous chloride, cupric chloride, manganese chloride; acidic resins, e.g. phenolic resins such as Bis-phenol A (4,4'-isopropylidene diphenol), para-phenyl phenol resin, para-octyl phenol resin, para-tertiary butyl phenol resin.

The solvent for the acidic co-reactant material must be chosen such that it has sufficient solubility for colour former and co-reactant material to enable the colour reaction to occur, and it must not substantially inhibit the colour reaction.

Moreover, the solvent should also preferably have a low volatility, which is essential if it is to be applied from a stamp pad. Other requirements are that it should be non-toxic, it should not possess a strong and/or unpleasant smell and of course it must be available commercially at a reasonable cost. Benzyl alcohol has been found to be a particularly suitable solvent. Solvents which are well known in the field of pressure-sensitive copying papers can possibly also be used, provided they meet the criteria set out above.

The pigmented ink is preferably a carbon black pigmented ink. We have found that carbon black can be satisfactorily dispersed in the acidic co-reactant solution provided a dispersant, for example oleic acid is used. A typical authenticating composition, given by way of example rather than limitation, is as follows:—

benzyl alcohol/zinc chloride
solution (saturated) 70 g.

carbon black (that supplied by
Coates Bros. as D829) 5 g

oleic acid (dispersant) 2.5 g

The composition just described will hereafter be referred to as the exemplified authenticating composition.

The filler may be a clay, for example the coating clay sold under the registered trade mark "SPS" by English China Clays Ltd. Other materials which are substantially inert to the colour former and to the acidic co-reactant can be used, for example "Dinkie A" (Registered Trade Mark) another clay sold by English China Clays Ltd., or finely calcium carbonate, e.g. in either precipitated or ground form. An example of such a calcium carbonate is that sold as Calopake (Registered Trade Mark) PC by John & E. Sturge Ltd.

Dinkie A clay may be disadvantageous with certain very reactive colour formers, for example that of which the formula is given in Example VII hereafter, in that it may lead to slight premature development of the colour of the colour

former. Thus, for use with certain colour formers it is preferable to use a calcium carbonate filler rather than a clay. If this is not possible or convenient, a less reactive colour former may have to be used, for example crystal violet lactone.

The particle size of the filler affects the flash-up time and the dusting characteristics of the filler. Three clays sold by English China Clays Ltd., Dinkie A of which 75% of the particles are of a size under $2\text{ }\mu\text{m}$, Grade B of which 45% of the particles are of a size under $2\text{ }\mu\text{m}$, and Grade E of which 25% of the particles are of a size under $2\text{ }\mu\text{m}$ were tested, and it was found that the susceptibility of the coated paper to dusting was about the same. However, the finer particle size clay improved the halo flash-up time. Thus if clay is used as the filler, it is preferably that at least 75% of the clay particles are of a size under $2\text{ }\mu\text{m}$. Moreover it was found that a further improvement in flash-up time without significant increased susceptibility to dusting was achieved by the addition of a fine particle size precipitated calcium carbonate, for example Calopake PC, in an amount of about 25% based on the clay content. This also enabled more casein to be incorporated in the coating mix without unacceptable slowing down of flash-up time, which in turn led to increased resistance to dusting. A further advantage of the addition of finely divided precipitated calcium carbonate was that the finished sheet was less susceptible to premature colouring by development of the colour former.

If a matting agent, for example Syloid (Registered Trade Mark) 266 was added to the clay, in the coating mix, there was a small improvement in flash-up time, but a reduction in resistance to dusting which more than outweighed the improved flash-up time.

The invention will now be illustrated by the following Examples:—

EXAMPLE I.

An aqueous coating composition containing by weight 85% of SPS coating clay, 4.5% of 3-chloro-6-cyclohexylamino fluoran and 10% of Jalan Eli (Registered Trade Mark) starch (sold by Laing-National Ltd.) was coated at about 20% solids onto document base paper, by means of a laboratory Meyer (Registered Trade Mark) bar coater. When an impression was applied to the coated paper by means of a metal stamp, carrying a saturated solution of zinc chloride in benzyl alcohol containing 6.6% by weight of a finely divided carbon black and 3.4% by weight of oleic acid, a black impression was immediately formed, and this impression was quickly surrounded by an orange halo.

EXAMPLE II.

The procedure described in Example I was repeated except that the aqueous coating composition contained by weight 88.5% SPS clay, 1.5% crystal violet lactone and 10% by weight of Jalan Eli starch. The halo in this case was blue.

EXAMPLE III.

The procedure described in Example II was repeated except that a different starch was used, namely that sold by CPC (United Kingdom) Ltd., under the name Amisol (Registered Trade Mark) Speciality Starch SO5731. A blue halo was again quickly formed.

EXAMPLE IV.

This example illustrates the use of a number of different colour formers with compositions containing different acidic co-reactants. In each case, document base paper was coated at 7 g/m^2 by means of a laboratory Meyer bar coater with the following coating composition:—

50	Colour former	0.3 g	}		50
	Water	29.7 g		*	
	Jalan Eli Starch	1.8 g	}		
	Water	60.0 g		**	
	SPS Clay	18.0 g			

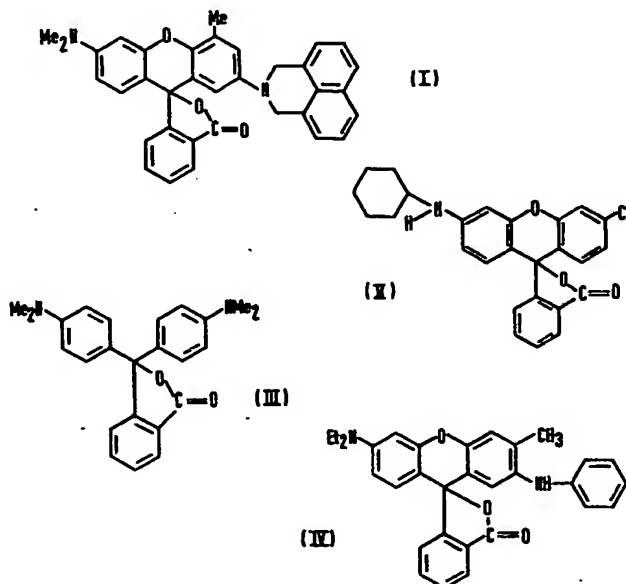
* 1% suspension by weight, colour former ball-milled for 24 hours.

** As starch solution.

The coating composition was aqueous at about 20% solids a 7 g/m² coating was applied. Four different colour formers were used, and these had formulae as follows:—

5

5



The various co-reactants used are detailed in the Table below, together with the details of the speed and intensity of the colour reaction which was obtained. In each case, the solvent for the co-reactant was benzyl alcohol.

Coreactant	Colour Formers							
	I		II		III		IV	
manganese chloride	I	S	1 sec	S	>4 sec	W	I	S
ferric chloride	1 sec	VS	I	VS	>4 sec	M	I	VS
cobaltous chloride	I	M	I	M	I	W	I	S
nickel chloride	I	S	2 sec	VW	2 sec	VW	I	M
cupric chloride	1 sec	VS	2 sec	S	I	M	1 sec	VS
zinc bromide	1 sec	VS	1 sec	VS	I	VS	I	VS
zinc nitrate	2 sec	S	2 sec	S	1 sec	VS	I	VS
zinc iodide	1 sec	VS	2 sec	S	1 sec	VS	I	VS
zinc chloride	1 sec	VS	1 sec	VS	I	VS	I	VS
p-toluene sulphonic acid	I	VS	I	VS	I	W	I	VS
benzene sulphonic acid	I	VW	-	-	-	-	I	W
sulphamic acid	I	M	I	W	I	W	I	W
sulphanilic acid	>4 sec	W	>4 sec	W	-	-	>4 sec	W
dodeca-tungstophosphoric acid	I	M	I	M	I	VW	I	S
d-tartaric acid	I	M	2 sec	VW	2 sec	VW	I	S
lactic acid	I	VS	I	W	I	W	I	VS
malonic acid	I	VS	I	M	I	M	I	S
maleic acid	I	VS	I	VS	I	S	I	VS
formic acid	I	VS	I	VS	I	S	I	VS
citric acid	I	S	I	W	2 sec	W	I	S

Coreactant	Colour Formers							
	I		II		III		IV	
chloroacetic acid	I	S	I	S	I	M	I	VS
acetic acid	I	S	I	W	2 sec	W	I	VS
dodeca-tungstosilicic acid	I	S	I	S	4 sec	W	I	VS
benzoic acid	I	VW	>4 sec	VW	—	—	I	W
tannic acid	I	M	>4 sec	VW	>4 sec	VW	I	M
succinic acid	I	S	I	W	>4 sec	W	I	M
stearic acid	>4 sec	M	>4 sec	W	—	—	I	W
adipic acid	I	M	>4 sec	VW	>4 sec	W	I	W
p-toluic acid	I	W	>4 sec	VW	>4 sec	W	I	W
2-naphthol-3,6-disulphonic acid	>4 sec	W	>4 sec	VW	—	—	I	W
1-naphthol-4-sulphonic acid	I	W	>4 sec	VW	—	—	I	W
PTBP resin	I	W	—	—	—	—	1 sec	W
PPP resin	I	VW	—	—	—	—	I	W
Bisphenol 'A'	I	W	—	—	4 sec	VW	I	W
POP resin	I	M	—	—	—	—	I	W

Key to Table:

- I — Instantaneous colour formation
 1 sec — Colour formation after 1 second
 VS — Very strong colour formation
 S — Strong colour formation
 M — Moderate colour formation
 W — Weak colour formation
 VW — Very weak colour formation
 — — No colour formation

It will be seen that the colour formers react differently to different co-reactants, and therefore that a particular authenticating composition is not necessarily suitable for use with all embodiments of the present security paper. It will however be appreciated that a skilled man can readily ascertain which combinations of co-reactants and colour formers are suitable for a particular purpose by routine experimentation.

EXAMPLE V.

This illustrates the use of a coating composition containing security chemicals, of the type previously mentioned herein.

3 g Jalan Ell starch were dissolved in 97 g water by heating, and a paste produced by mixing 4.86 g diphenyl guanidine and 2.45 g glacial acetic acid was stirred into the hot starch solution.

100 g of a 4% suspension of crystal violet lactone in water were then stirred in followed by 0.12 g of Orasol (Registered Trade Mark) solvent sensitive black dye and 43 g SPS clay. The crystal violet lactone suspension had been ball-milled for 24 hours. The composition thus produced was coated on to document base paper at 7 g/m² and the coated paper thus produced was then stamped with the authenticating composition exemplified previously. A blue halo formed rapidly about the black impression thus produced, and black speckles were present within the halo.

EXAMPLE VI.

This illustrates the production of the present security paper by coating on a pilot plant scale rather than in the laboratory. A coating composition was made up as follows:—

430 g of Calgon (Registered Trade Mark) PT dispersant were dissolved in 19 kg of water in a blunger. A suspension of 4 kg crystal violet lactone in 15 kg water containing 140 g Nopco (Registered Trade Mark) 1407/50 antifoamer was added. The crystal violet lactone suspension had been attrited for 3 hours in a Torrance IS attritor.

200 g of Orasol black solvent sensitive dye was added slowly, so as to ensure good dispersion.

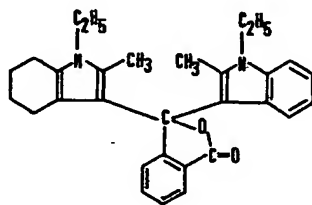
1 kg of a security chemical sold as "Vulcafor" by I.C.I. Limited was made into a paste with 500 ml of glacial acetic acid and added to a hot starch solution in a starch cooker. The starch solution had been made by dissolving 3 kg of Jalan Ell starch in 50 kg water. The mixture in the cooker was allowed to cook and its pH was adjusted to 6 with ammonia solution, and the mix then added to the mixture already in the blunger.

43 kg of Dinkie A clay was then added slowly so as to permit good dispersion. The pH was then adjusted to 6.8, and the dispersion was adjusted to 30% solids, which resulted in a viscosity of 550 cP. The resulting mixture was then coated onto a 49 g/m² base paper by means of an air-knife coater.

On stamping with the authenticating composition exemplified previously, a blue halo was obtained, and black speckles were present with the halo.

EXAMPLE VII.

The procedure of Example VI was then repeated, except that the colour former was of the formula:—



A red halo was obtained. It was noticed that the coated paper had a pinkish tinge before authentication, presumably of premature development of the colour former, which is very sensitive, by the clay, which is slightly acidic. This explanation is supported by the observation that such a tinge was not obtained if Dinkie A clay was replaced by finely precipitated inert calcium carbonate (Calopake PC). The pinkish tinge could also be avoided if a lower level of colour was used.

WHAT WE CLAIM IS:—

1. A method of authenticating a document, wherein the document is printed on a security paper comprising a paper base coated with a composition containing a leucodye colour former, an inert filler and a binder, and is authenticated by stamping with an authenticating composition comprising a mixture of a pigmented dark ink and a solution of an acidic material which reacts with the leucodye colour former to develop a colour.
2. A method as claimed in Claim 1, wherein the coating composition also contains a security chemical to give protection against forgery.
3. A method as claimed in Claim 1 or Claim 2, wherein the binder is casein.
4. A method as claimed in Claim 3, wherein from 12 to 13 parts of casein are present per 100 parts of filler.
5. A method as claimed in any one of the preceding Claims, wherein the filler comprises a clay.
6. A method as claimed in Claim 5, wherein 75% of the clay particles have a diameter of 2 μm or less.
7. A method as claimed in any one of the preceding claims, wherein the filler comprises a finely divided calcium carbonate.
8. A method as claimed in Claims 5 or 6 and Claim 7, wherein the filler comprises by weight 75% clay and 25% finely divided calcium carbonate.
9. A method as claimed in any one of the preceding Claims, wherein the colour former has a mean particle diameter of 3 to 4 μm .
10. A method as claimed in any one of the preceding Claims, wherein the coating composition is applied by spot printing.
11. A method as claimed in any one of the preceding Claims, wherein the acidic material is dissolved in benzyl alcohol.
12. A method of authenticating a document according to Claim 1, substantially as hereinbefore described.
13. In combination, a document to be authenticated and an authenticating composition which can be applied by stamping so as to produce a distinctive marking to authenticate said document, wherein the document is printed on a security paper comprising a paper base coated with a composition containing a leucodye colour former, an inert filler and a binder, and the authenticating composition comprises a mixture of a pigmented dark ink and a solution of an acidic material which reacts with the leucodye colour frame to develop a colour.
14. A combination as claimed in Claim 13, wherein the coating composition also contains a security chemical to give protection against forgery.
15. A combination as claimed in Claim 13 or Claim 14, wherein the binder is casein.
16. A combination as claimed in Claim 15, wherein from 12 to 13 parts of casein are present per 100 parts of filler.
17. A combination as claimed in any one of Claims 13 to 16, wherein the filler comprises a clay.
18. A combination as claimed in Claim 17, wherein 75% of the clay particles have a diameter of 2 μm or less.
19. A combination as claimed in any one of Claims 13 to 18, wherein the filler comprises a finely divided calcium carbonate.
20. A combination as claimed in Claims 17 or 18 and Claim 19, wherein the filler comprises by weight 75% clay and 25% finely divided calcium carbonate.
21. A combination as claimed in any of Claims 13 to 20, wherein the colour former has a mean particle diameter of 3 to 4 μm .
22. A combination as claimed in any one of Claims 13 to 21, wherein the coating composition is applied by spot printing.
23. A combination as claimed in any one of Claims 13 to 22, wherein the acidic material is dissolved in benzyl alcohol.
24. A combination according to Claim 13, substantially as hereinbefore described.

PAGE, WHITE & FARRER,
Chartered Patent Agents,
27 Chancery Lane,
London WC2A 1NT.
Agents for the Applicants.